



PECASE 08) - ION-CONDUCTING NETWORK MEMBRANES USING TAPERED BLOCK COPOLYMERS

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**07/08/2015
Final Report**

DISTRIBUTION A: Distribution approved for public release.

**Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ RTD
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REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 14-07-2015		2. REPORT TYPE Final Performance		3. DATES COVERED (From - To) 30-09-2009 to 30-03-2015	
4. TITLE AND SUBTITLE ION-CONDUCTING NETWORK MEMBRANES USING TAPERED BLOCK COPOLYMERS				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA9550-09-1-0706	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Thomas Epps				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UNIVERSITY OF DELAWARE 220 HULLIHEN HALL NEWARK, DE 19716 US				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AF Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT A DISTRIBUTION UNLIMITED: PB Public Release					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT <p>The major purpose of this proposal was to design, synthesize, and characterize new nanostructured polymer electrolytes for rechargeable lithium battery membranes using tapered block copolymers. Tapered block copolymers possess the ability to tune nanostructure, processing temperatures, and mechanical properties independent from chemical constituents and copolymer block segregation strength by manipulating the interfacial profile in the self-assembled nanostructures. The key outcomes of the completed proposal included: 1) generating nanoscale networks [such as the gyroid network] in tapered block copolymer self-assemblies to improve conductivity by 500x over non-cocontinuous nanostructures; 2) improving room-temperature conductivity by 150x through the incorporation of non-crystallizing PEO-like conducting domains; 3) improving all-temperature conductivity by ~5x through the use of tapers to lower the glass transitions temperatures in the conducting polymer domains, thereby increasing chain mobility; 4) demonstrating the ability of tapering to tune network formation in various lithium salt counterion systems through adjustments in the taper profile in order to maximize conductivity; 5) improving mechanical properties through the formation of nanoscale network domains; 6) preliminary testing of battery cyclability at various currents to demonstrate ability to achieve near-theoretical capacities at well over 100 cycles of performance lifetime.</p>					
15. SUBJECT TERMS ION-CONDUCTING, TAPERED					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF	19a. NAME OF RESPONSIBLE PERSON Thomas Epps
a. REPORT	b. ABSTRACT	c. THIS PAGE			
Standard Form 298 (Rev. 8/98) Prescribed by ANSI Std. Z39.18					

U	U	U	UU	PAGES	19b. TELEPHONE NUMBER (Include area code) 302-831-0215
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Accomplishments

The key outcomes since the last report include: 1) generating nanoscale networks [such as the gyroid network] in tapered block copolymer self-assemblies to improve conductivity by 500x over non-cocontinuous nanostructures; 2) improving all-temperature conductivity by ~5x through the use of tapers to lower the glass transitions temperatures in the conducting polymer domains, thereby increasing chain mobility; 3) demonstrating the ability of tapering to tune network formation in various lithium salt counterion systems through adjustments in the taper profile in order to maximize conductivity; 4) improving mechanical properties through the formation of nanoscale network domains; 5) preliminary testing of battery cyclability at various currents to demonstrate ability to achieve near-theoretical capacities at well over 100 cycles of performance lifetime. Further details are provided in the following two paragraphs.

The influence of tapered interfaces on the nanoscale morphologies of ion-doped poly(styrene-*b*-*oligo*-oxyethylene methacrylate) block polymers was explored. Most significantly, the location of double gyroid network phase window was found in ion-doped normal-tapered materials, and a similar window was not detectable in the corresponding non-tapered and inverse-tapered polymers. Additionally, the effective interaction parameters, χ_{eff} , were reduced substantially in the tapered materials in comparison to their non-tapered counterparts, indicating an ability to process these battery materials at lower temperatures, with less solvent, and over shorter time scales. Thus, it was demonstrated that tapering between polymer blocks provided unique control over block polymer morphologies and improved the material processability (due to lower χ_{eff}), potentially facilitating the development of future ion-conducting devices.

Additionally, the design and conductivity testing of novel solid electrolytes using tapered block polymers (TBPs) was conducted. TBPs were synthesized *via* atom transfer radical polymerization (ATRP) consisting of rigid polystyrene and ion-conducting poly(*oligo*-oxyethylene methacrylate) segments, and the role of tapered interfaces on ion transport was explored. It was shown that the taper profile and taper volume fraction significantly impact the glass transition temperatures (T_g s) in block polymer electrolytes, thus affecting the ionic conductivity. Additionally, it was discovered that the normal-tapered materials with ~60 vol% tapering exhibit remarkable improvements in ionic conductivity (increase ~190% at 20 °C and increase ~90% at 80 °C) in comparison to their non-tapered counterparts. Thus, the TBPs, with controllable interfacial interactions, indicated an exciting opportunity for the fabrication of cost-effective, highly-efficient, and stable energy storage membranes.

In a collaboration with the Jiao group in the Department of Chemical and Biomolecular Engineering at the University of Delaware, initial attempts for the battery prototype based on BP electrolytes were conducted using a lithium metal anode and a lithium iron phosphate (LiFePO₄) as an active material for the cathode. The composite cathode was prepared by mixing P(S-EO) with carbon black and LiFePO₄ in *N*-methyl-2-pyrrolidone (NMP). The polymer electrolyte was prepared by mixing P(S-EO) and lithium bis(trifluoromethanesulfonyl)imide [LiTFSI] at a salt-doping ratio of [EO]:[Li] = 12:1. Example cycle-life data for the Li/P(S-EO)/LiFePO₄ cell is shown in Figure 1. The specific discharge capacity was ~100–150 mAh/g (theoretical capacity 170 mAh/g). However, the preliminary result shows no capacity fading at three different discharge rates, indicating good cycling stability. This investigation currently is in progress.

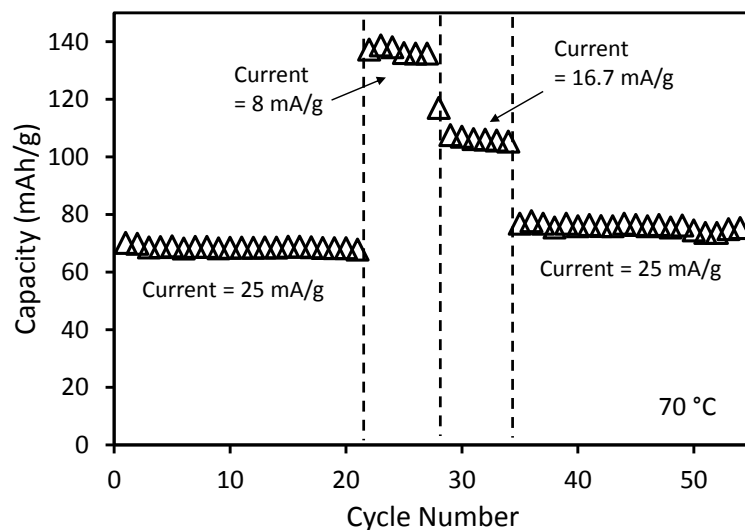


Figure 1: Cycle-life data for the Li/P(S-EO)/LiFePO₄ cell at 70 °C. The reported data are the specific discharge capacities calculated based on the mass of the active materials.

Project Summary

The major purpose of this project was to design, synthesize, and characterize new nanostructured polymer electrolytes for rechargeable lithium battery membranes using tapered block copolymers. Tapered block copolymers possess the ability to tune nanostructure, processing temperatures, and mechanical properties independent from chemical constituents and copolymer block segregation strength by manipulating the interfacial profile in the self-assembled nanostructures. The key outcomes of the completed project included: 1) generating nanoscale networks [such as the gyroid network] in tapered block copolymer self-assemblies to improve conductivity by 500x over non-cocontinuous nanostructures; 2) improving room-temperature conductivity by 150x through the incorporation of non-crystallizing PEO-like conducting domains; 3) improving all-temperature conductivity by ~5x through the use of tapers to lower the glass transitions temperatures in the conducting polymer domains, thereby increasing chain mobility; 4) demonstrating the ability of tapering to tune network formation in various lithium salt counterion systems through adjustments in the taper profile in order to maximize conductivity; 5) improving mechanical properties through the formation of nanoscale network domains; 6) preliminary testing of battery cyclability at various currents to demonstrate ability to achieve near-theoretical capacities at well over 100 cycles of performance lifetime.

The following sections detail some of the key milestones that allowed the successful achievement of the outcomes mentioned above. Further details, including experimental equipment, set up, procedures, and data can be found in the archival publications, supporting information, and theses generated as a part of this work.

To prepare for the design of ion-conducting and tapered block copolymers for battery membranes, an initial task was to generate network-forming and tapered block polymers in non-conducting systems. Thus, this work reported, for the first time, the synthesis of interfacially-manipulated ABC triblock copolymers using a combination of anionic polymerization, ATRP, and Huisgen 1,3-dipolar cycloaddition click chemistry. The tapered block polymer generated through this route, containing segments styrene (S), isoprene (I), and methyl methacrylate (M) with isoprene/styrene and styrene/methyl methacrylate tapers, formed an alternating gyroid network upon self-assembly in bulk (membrane) geometry (see Figure 1). This result suggested that it was possible to modify the interfacial composition profile between the pure blocks in linear triblock copolymers, while still retaining the complex co-continuous nanostructures that are a hallmark of triblock copolymers. Though the approach was applied to ABC triblock copolymers, a similar methodology can be employed to generate tapered tetrablock and pentablock copolymers, as well as ABA triblock copolymers with different tapered profiles at each A-B junction. Finally, the protocols allowed for the design and synthesis of new nanostructured materials with a wide variety of components such as the battery materials described below. (publication #5)

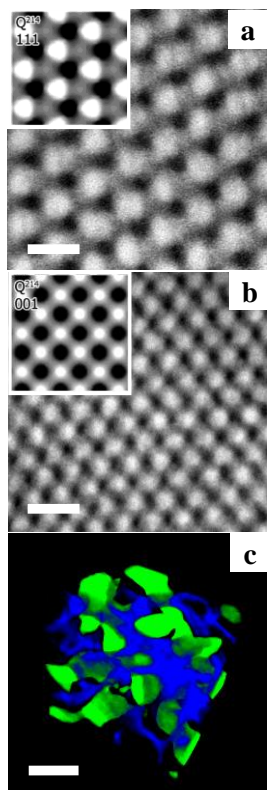


Figure 1. Transmission electron microscopy (TEM) micrographs and TEM tomography image for P(I-IS-SM-M). (a) and (b) Experimental TEM images, representing the reflection planes [111] and [001], respectively. The inset images are simulated TEM micrographs. Dark domains correspond to OsO₄-stained PI. Scale bars represent 50 nm. (c) 3-D reconstructed image. Only PI (blue) and PMMA (green) domains are shown for clarity. Scale bar represents 30 nm.

Concurrent with the above effort, it was demonstrated that a new mixed-salt methodology could be used to increase the room temperature ionic conductivities of block copolymer solid electrolytes. These electrolyte systems are especially suitable in solid-state lithium batteries, in which a thermally, electrochemically, and mechanically stable electrolyte membrane with high ionic conductivity over a wide temperature range is needed. Using a mixed-salt system of LiClO₄ and LiTFSI, it was found that the melting temperatures and degrees of crystallinity of the crystalline phases could be decreased in the PS-PEO system at [EO]:[Li] = 6:1. This reduction in melting temperature and crystallinity enabled the achievement of higher ionic conductivities at low temperatures compared to corresponding single-salt-doped PS-PEO electrolytes. It also was found that the mixed-salt system showed no benefit on decreasing the melting point and crystallinity at [EO]:[Li] = 12:1 because the crystallization behavior in the 12:1 system was dominated by the PEO crystalline phase, which showed preferential crystallization compared to the P(EO)₆:LiClO₄ and P(EO)₆:LiTFSI phases and ultimately drove the decrease in ionic conductivity at this salt doping level. The results suggested that the use of a mixed-salt system could lead to a higher room temperature ionic conductivity in the appropriate block copolymer electrolyte systems. Additionally, the work showed that mixed salts could influence copolymer energetics by estimating the χ_{eff} values in our lamellae-forming PS-PEO system using the domain spacing data from SAXS and the relationship between domain spacing and χ for block copolymers in the strong segregation regime. The LiTFSI-doped block polymer system and the LiClO₄-doped block polymer system showed similar slopes (χ_{eff} vs. salt concentration), which were attributed to the close Lewis acidities of LiTFSI and LiClO₄. (publication #2)

While mixed-salts demonstrated one approach for improving conductivity, it also was necessary to demonstrate the advantages of 3-D conducting pathways. Thus, the advantages of block copolymer systems with 3-D conducting pathways for electrolyte membranes were shown by examining the conductivity profiles of LiClO₄-doped PS-PEO samples with various morphologies. To analyze the morphologies of block copolymer electrolytes, a flow alignment technique was applied to align the domains of the sample. Three morphologies, lamellae (LAM), hexagonally perforated lamellae (HPL), and hexagonally-packed cylinders (HEX), were obtained by slightly changing f_{PEO} from 0.70 to 0.75. Additionally, for a LAM-forming sample, it was found that the moderate shear created during hot-pressing can orient domains against the conducting direction decreasing the conductivity as much as two and half times. However, for a hot-pressed HEX-forming sample, conductivity was not affected by the domain orientations due to the 3-D conducting pathways of the PEO matrix (see Figure 2). The results showed that the normalized conductivity increased dramatically upon a morphology change from LAM (2-D conducting pathways) to HPL/HEX (3-D conducting pathways) even when the PEO molecular weight and non-uniform domain orientation effects were considered. These results for samples larger than 40 kg/mol differed from those reported for low molecular weight PS-PEO systems. (publication #7)

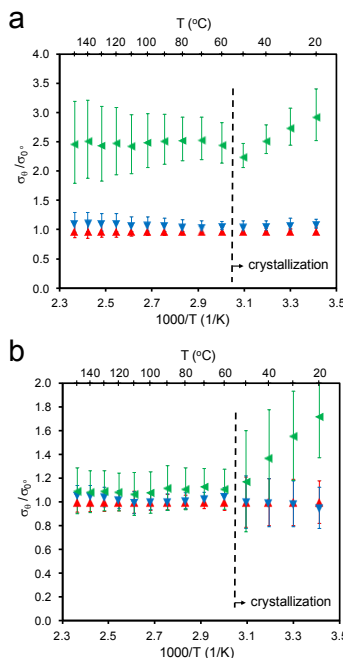


Figure 2. Ionic conductivity profiles of (a) SO₇₀P24 (LAM) and (b) SO₇₅P24 (HEX) for various sample orientations. Sample preparation is described in the Experimental section. The ionic conductivities of samples following the hot-pressing procedure (as shown in Figure 5) are denoted as σ_{0° and normalized to 1 (red upward triangle, ▲). Samples after the first conductivity measurement were then cut to ~ 0.5 mm wide strips, turned 180° or 90°, re-packed into Teflon O-ring, and re-measured for conductivity. Conductivities of samples turned 180° and 90° are denoted as σ_{180° (blue downward triangle, ▼) and σ_{90° (green leftward triangle, ◀), respectively. The crystallization regions indicate the existence of semi-crystalline PEO domains. NOTE: the conductivities in each panel have a separate normalization. The overall (non-normalized) conductivity of the HEX samples is approximately 5x higher than that for the LAM samples.

In this project, it also was illustrated that the self-assembly of lithium ion-doped P(S-OEM) BPs and TBPs exhibits a strong dependence on the presence of tapered interfaces, the profile of the tapers (normal or inverse), and the concentration of lithium ions. Of particular importance is the

experimental discovery of a double gyroid network phase window in the ion-doped, normal-tapered system despite the fact that no network morphologies were detected in the non-tapered and inverse-tapered materials. Moreover, this project showed that tapered interfaces present a promising strategy for reducing the polymer–polymer interactions and polymer chain stretching upon lithium ion addition. The highlighted results (samples of which are shown in Figures 3 and 4) suggested an advanced design pathway for the next generation of nanostructured and highly-processable materials in transport applications. (publication #13)

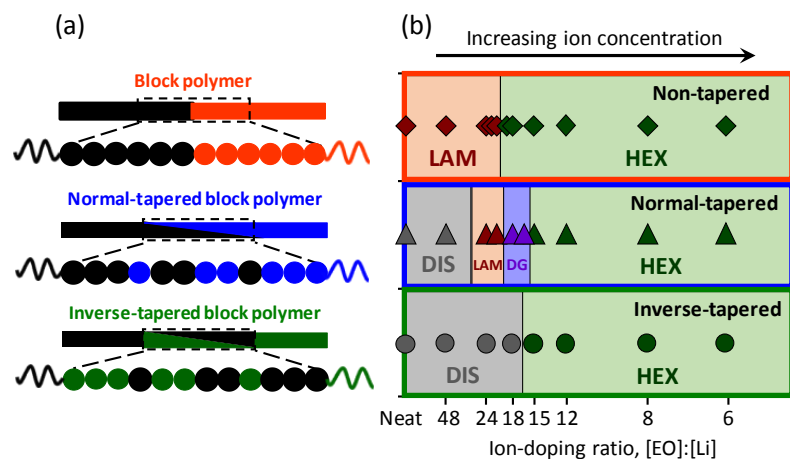


Figure 3. (a) Illustration of non-tapered, normal-tapered, and inverse-tapered BPs. (b) Phase behavior of non-tapered P(S-OEM), normal-tapered P(S-SOEM-OEM), and inverse-tapered P(S-OEMS-OEM) BPs as a function of the ion-doping ratio. LAM: lamellae; HEX: hexagonally-packed cylinder; DIS: disordered phase; DG: double gyroid.

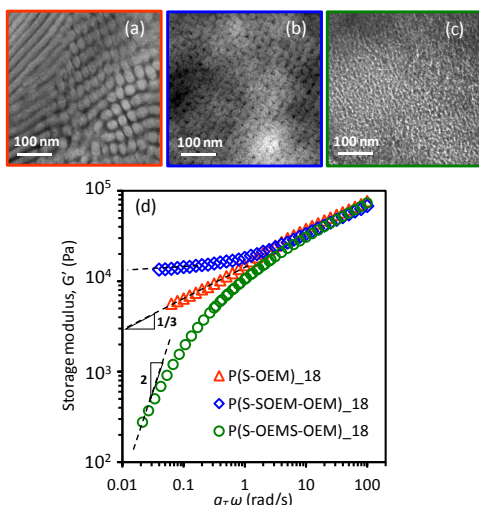


Figure 4. TEM images for LiCF_3SO_3 -doped polymers at $[\text{EO}]:[\text{Li}] = 18:1$: (a) $\text{P}(\text{S-OEM})$; (b) $\text{P}(\text{S-SOEM-OEM})$; (c) $\text{P}(\text{S-OEMS-OEM})$. TEM specimens were cut into ≈ 70 nm slices from the thermally annealed SAXS samples at -120 °C on a cryo-microtome. The POEM domains were stained preferentially with RuO_4 vapor to enhance domain contrast prior to imaging. (d) Isothermal frequency sweeps for 18:1 LiCF_3SO_3 -doped $\text{P}(\text{S-OEM})$ at 110 °C and 18:1 LiCF_3SO_3 -doped TBPs. 8 mm diameter parallel plates were utilized for the DMA experiments. Data were collected at a strain of 3%, and the DMA results for both TBPs were shifted according to time-temperature superposition using a reference temperature of 70 °C. Dash lines are included for visual clarity of the terminal responses. The number in the legend represents the $[\text{EO}]:[\text{Li}]$ ion-doping ratio for the sample. The brightness in (c) was enhanced for visual clarity.

To culminate the currently published aspects of the project, tapered block polymer electrolytes, based on $\text{P}(\text{S-OEM})$ block polymers, were prepared for the first time. This new family of nanostructured polymer electrolytes provided a unique approach for tuning thermal and transport properties at constant molecular mass and chemical composition. Of particular importance, the tapered interfaces presented an excellent ability to manipulate T_g of BP electrolytes through adjustments in the taper profile and taper volume fraction, thus enabling the ability to design materials with tailored and highly improved conductivity. This interfacial modification approach for polymer electrolytes offers an avenue for solving the dueling problems of efficiency and cost in current electrolytes and displays promising potential for energy storage devices. Details of the conductivity improvements in response to tapering are demonstrated in Figures 5 and 6. (publication #14)

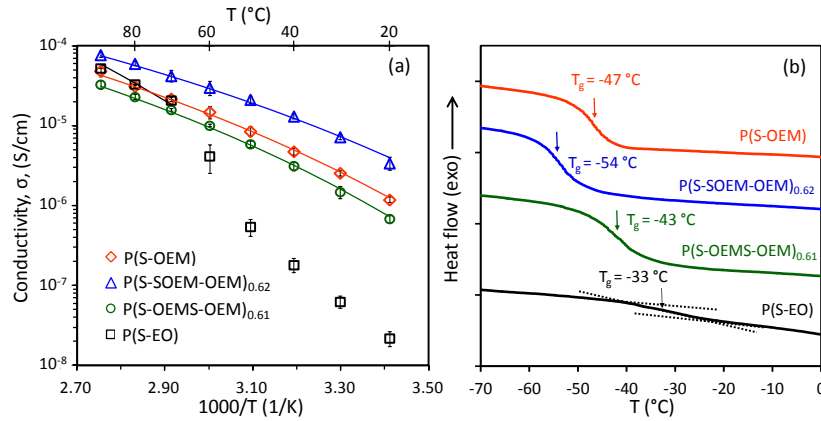


Figure 5. (a) Ionic conductivity profiles for LiCF_3SO_3 -doped P(S-OEM), P(S-SOEM-OEM)_{0.62}, P(S-OEMS-OEM)_{0.61}, and P(S-EO) at $[\text{EO}]:[\text{Li}] = 15:1$. The reported values are averages from three samples with standard deviations indicated by error bars on the data points. The solid lines are VFT fits to the conductivity data. (b) Third-heating DSC traces of LiCF_3SO_3 -doped P(S-OEM), P(S-SOEM-OEM)_{0.62}, P(S-OEMS-OEM)_{0.61}, and P(S-EO) at $[\text{EO}]:[\text{Li}] = 15:1$. The heating rate was 10 °C/min for all samples. The DSC traces were shifted vertically for clarity. The T_g value was determined from the midpoint of the inflection in the third heating trace.

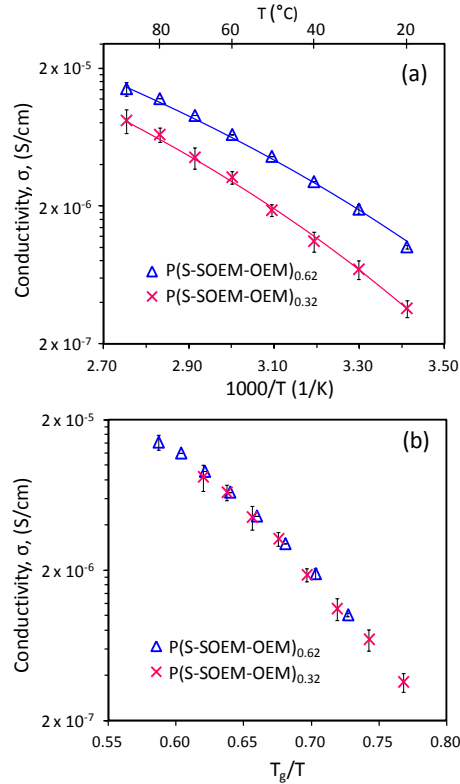


Figure 6. (a) Temperature-dependent conductivity profiles and (b) normalized ionic conductivity profiles for LiCF_3SO_3 -doped P(S-SOEM-OEM)_{0.62} and LiCF_3SO_3 -doped P(S-SOEM-OEM)_{0.32} at $[\text{EO}]:[\text{Li}] = 24:1$. The reported values of ionic conductivity are averages from three samples with standard deviations indicated by error bars on the data points. The solid lines in (a) are VFT fits.

Executive Summary

This research effort culminated in the production of two student Ph.D. theses.

1. Wen-Shiue Young - Ion-conductivity in Block Copolymer Electrolyte Membranes - 04/03/2012 *Dow Chemical*

Understanding the factors that affect copolymer's morphological and electrical behavior upon salt-doping is important for the design and optimization of battery electrolyte materials. This thesis explored the morphological, thermal, and electrical behavior of salt-doped poly(styrene-*b*-ethylene oxide) (PS-PEO) systems. While PS provides mechanical integrity, PEO forms PEO:salt complexes that enable ion transport. The morphologies and domain spacings of salt-doped PS-PEO samples were characterized using small-angle X-ray scattering and transmission electron microscopy, while the crystallinities of PEO:salt complexes and ionic conductivities of the electrolytes were examined via differential scanning calorimetry and AC impedance spectroscopy, respectively. First, the salt-doping effects on the phase behavior of PS-PEO block copolymers were studied by doping various lithium salts over a range of [EO]:[Li] ratios. It was found that copolymer microstructure can be tuned by changing the Li counterion and the salt doping ratio. The effective interaction parameter, χ_{eff} , of the salt-doped copolymer was estimated using strong segregation theory and the domain spacings obtained from SAXS. χ_{eff} was found to have a linear relationship with salt concentration, and the slope depended on the counterion. Additionally, thermal order-order transitions caused by the crystallization of confined PEO-lithium complexes were probed. Second, using a mixed-salt system, LiClO₄/LiTFSI, the room temperature conductivity was improved by more than an order of magnitude due to the coinhibition of crystallite growth by the concerted behavior of the PEO:LiClO₄ and PEO:LiTFSI phases. Finally, 3-D conducting pathways were found to exhibit significantly higher normalized ionic conductivity than the 2-D conducting pathway. These results also suggested that using block copolymer electrolytes with 3-D conducting pathways can prevent a decrease in through-plane conductivity caused by the partial nanostructure alignment during sample preparation. In addition to improving the design and optimizing the electrical performance of block copolymer electrolytes, the methods developed in this work can be extended to other applications that require adjustment of copolymer domain spacing such as nanotemplating and nanoporous membranes.

Thesis available from the University of Delaware Library

2. Wei-Fan Kuan - Interfacial-Modified Block Polymers for Lithium Battery Electrolytes - 05/21/2015

Block polymer electrolytes have become increasingly attractive for lithium-based battery applications due to their low volatility, sufficient mechanical strength, and thermal and electrochemical stability in comparison to conventional liquid electrolytes. However, current BP electrolytes suffer from poor conductivity near room temperatures (due to polymer crystallization) and high processing costs (due to unfavorable polymer-polymer interactions). To overcome the above limitations, this dissertation proposed a design of new BP electrolytes with a specific focus on network nanostructures using tapered block polymers (TBPs). The work presented in this dissertation examined the morphological, thermal, and electrical properties of TBPs. Incorporating a taper interface in BPs was found to reduce the unfavorable polymer-polymer interactions and stabilize additional morphologies in salt-doped BPs. Most significantly, a double gyroid network window was located in the salt-doped normal-tapered system. Additionally, the tapered interfaces demonstrated a unique handle for manipulating the glass transition temperature (T_g) of BP electrolytes through adjustments in the taper profile and taper volume fraction, thus enabling control over the ionic conductivity. Finally, a novel synthetic strategy for generating dual-tapered triblock terpolymers was presented. An alternating gyroid-forming tapered triblock terpolymer was generated, showing the ability to

retain network structures in dual-tapered BP systems. Overall, the approaches presented in this dissertation provide the opportunity to design cost-effective, highly-efficient, and stable energy storage devices.

Thesis to be available from the University of Delaware Library

The cumulative list of publications is found in the archival publications section of this report.

The major participants involved in this research effort include:

Prof. Thomas H. Epps, III (PI)

Dr. Matthew Green (postdoctoral researcher)

Dr. Sung Hyun Han (postdoctoral researcher)

Wei-Fan Kuan (Ph.D. student)

Melody Morris (Ph.D. student)

Jong Keun Park (postdoctoral researcher)

Maeva Tureau (Ph.D. student)

Bin Wei (graduate assistant)

Wen-Shiue Young (Ph.D. student)

1.

1. Report Type

Final Report

Primary Contact E-mail**Contact email if there is a problem with the report.**

martar@udel.edu

Primary Contact Phone Number**Contact phone number if there is a problem with the report**

302-831-0181

Organization / Institution name

University of Delaware

Grant/Contract Title**The full title of the funded effort.**

(PECASE 08) - ION-CONDUCTING NETWORK MEMBRANES USING TAPERED BLOCK COPOLYMERS

Grant/Contract Number**AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".**

FA9550-09-1-0706

Principal Investigator Name**The full name of the principal investigator on the grant or contract.**

Thomas H. Epps, III

Program Manager**The AFOSR Program Manager currently assigned to the award**

Dr. Charles Lee

Reporting Period Start Date

09/30/2009

Reporting Period End Date

03/30/2015

Abstract

The major purpose of this proposal was to design, synthesize, and characterize new nanostructured polymer electrolytes for rechargeable lithium battery membranes using tapered block copolymers. Tapered block copolymers possess the ability to tune nanostructure, processing temperatures, and mechanical properties independent from chemical constituents and copolymer block segregation strength by manipulating the interfacial profile in the self-assembled nanostructures. The key outcomes of the completed proposal included: 1) generating nanoscale networks [such as the gyroid network] in tapered block copolymer self-assemblies to improve conductivity by 500x over non-cocontinuous nanostructures; 2) improving room-temperature conductivity by 150x through the incorporation of non-crystallizing PEO-like conducting domains; 3) improving all-temperature conductivity by ~5x through the use of tapers to lower the glass transitions temperatures in the conducting polymer domains, thereby increasing chain mobility; 4) demonstrating the ability of tapering to tune network formation in various lithium salt counterion systems through adjustments in the taper profile in order to maximize conductivity; 5) improving mechanical properties through the formation of nanoscale network domains; 6) preliminary testing of battery cyclability at various currents to demonstrate ability to achieve near-theoretical capacities at well over 100 cycles of performance lifetime.

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Archival Publications (published) during reporting period:

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1. [17] Roy, R.; Park, J. K.; Young, W.; Mastroianni, S.; Tureau, M. S.; Epps, T. H., III. *Macromolecules*, 2011, 44(10), 3910-3915. "Double-Gyroid Network Morphology in Tapered Diblock Copolymers." (corresponding author)
2. [22] Young, W.; Albert, J. N. L.; Schantz, A. B.; Epps, T. H., III, *Macromolecules*, 2011, 44(20), 8116-8123. "Mixed-salt Effects on the Ionic Conductivity of Lithium-doped PEO-containing Block Copolymers." (corresponding author)
3. [47] Albert, J. N. L.; Young, W.; Lewis, R. L., III; Bogart, T. D.; Smith, J; Epps, T. H., III, *ACS Nano* 2012, 6(1), 459-466. "Systematic Study on the Effect of Solvent Removal Rate on the Morphology of Solvent Vapor Annealed ABA Triblock Copolymer Thin Films." (corresponding author)
4. [15] Labiano, A.; Dai, M.; Young, W.-S.; Stein, G.; Cavicchi, K.; Epps, T. H. III; Vogt, B., *Journal of Physical Chemistry C* 2012, 116, 6038-6046. "Impact of Homopolymer Pore Expander on the Morphology of Mesoporous Carbon Films using Organic-Organic Self-Assembly."
5. [12] Kuan, W. F.; Roy, R.; Rong, L.; Hsiao, B.; Epps, T. H., III, *ACS Macro Letters* 2012, 1, 519-523. "Design and Synthesis of Network-Forming Triblock Copolymers Using Tapered Interfaces." (corresponding author)
Highlighted in ACS Noteworthy Chemistry online
6. [9] Labiano, A.; Dai, M.; Taylor, D.; Young, W.-S.; Epps, T. H., III, Rege, K.; Vogt, B. D., *Microporous and Mesoporous Materials* 2012, 160, 143-150. "Slow Release Kinetics of Mitoxantrone from Ordered Mesoporous Carbon Films."
7. [33] Young, W.; Epps, T. H., III, *Macromolecules* 2012, 45(11) 4689-4697. "Ionic Conductivities of Block Copolymer Electrolytes with Various Conducting Pathways: Sample Preparation and Processing Considerations." (corresponding author)
8. [6] Tureau, M. S.; Kuan, W. F.; Rong, L.; Hsiao, B. H.; Epps, T. H., III, *Macromolecules* 2012, 45(11), 4599-4605. "Inducing Order from Disordered Copolymers: On Demand Generation of Triblock Morphologies Including Networks." (corresponding author)
9. [9] Mayeda, M. K.; Kuan, W. F.; Young, W. S.; Lauterbach, J. A.; Epps, T. H., III, *Chemistry of Materials*

2012, 24(14), 2627-2634. "Controlling Particle Location with Mixed Surface Functionalities in Block Copolymer Thin Films." (corresponding author)

10. [6] Tureau, M. S.; Epps, T. H., III, *Macromolecules* 2012, 45(20) 8347-8355. "Effect of Partial Hydrogenation on the Phase Behavior of Poly(isoprene-b-styrene-b-methyl methacrylate Triblock Copolymers)." (corresponding author)

11. [24] Young, W. S.; Kuan, W. F.; Epps, T. H., III, *Journal of Polymer Science: Part B - Polymer Physics* 2014, 52(1), 1-16. ([invited review article]) "Block Copolymers for Rechargeable Lithium Batteries." (corresponding author)

Inside Cover Article

12. [1] Cho, W.; Wu, J.; Shim, B. S.; Kuan, W. F.; Mastroianni, S. E.; Young, W. S.; Kuo, C.C.; Epps, T. H., III, Martin, D. C. *Physical Chemistry Chemical Physics* 2015, 17, 5115-5123. "Synthesis and Characterization of Bicontinuous Cubic Poly(3,4-ethylene dioxythiophene) Gyroid (PEDOT GYR) Gels"

13. [2] Kuan, W. F.; Remy, R.; Mackay, M. E.; Epps, T. H., III *RSC Advances* 2015, 5, 12597-12604. [invited special issue on electrochemical storage] "Controlled Ionic Conductivity via Tapered Block Polymer Electrolytes" (corresponding author)

14. [0] Kuan, W. F.; Nguyen, N. A.; Reed, E. H.; Mackay, M. E.; Epps, T. H., III *MRS Communications* 2015 [invited special issue on polymers and soft matter] "Using Tapered Interfaces to Manipulate Nanoscale Morphologies in Ion-Doped Block Polymers" (corresponding author) DOI: 10.1557/mrc.2015.19

Non Peer-Reviewed Work

1. Young, W.S., Epps, T.H. III; "Salt doping in PEO-containing block copolymers: counterion and concentration effects." *ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY*, March 2009, Salt Lake City, UT, *PMSE Preprints* (2009), 100, 274-275

2. Wu, J., Young, W.-S., Epps, T., & Martin, D. C. (2010). Electrical and structural changes during phase transitions in conducting polymer cubic phases. *Bulletin of the American Physical Society*, 55(2), C1.00005.

3. Epps, T.H., III., Roy, R., Park, J.K., Kuan, W.F. "Manipulating the Interfacial Regions of Self-Assembled Block Copolymer Structures" *ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY*, Volume: 241, Pages: 259-PMSE March 2011, Anaheim, CA, *PMSE Preprints* 2011

4. Epps, T. H., III. "Designer nanoscale materials: Interfacial manipulations in block copolymer systems" *ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY*, March 2012, San Diego, CA, *POLY Preprints* 2012, accepted

5. Kuan, W.F., Roy, R., Epps, T. H., III. "Interfacial modification in self-assembled triblock copolymers" *ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY*, March 2012, San Diego, CA, *POLY Preprints* 2012, accepted

Patents and Patent Applications

Wei-Fan Kuan and Thomas H. Epps, III, "Tapered Block Copolymer Electrolytes." U.S. Pat. Appl. 14592441 filed on Jan. 8, 2015

Theses Supervised

1. Wen-Shiue Young - Ion-conductivity in Block Copolymer Electrolyte Membranes - 04/03/2012 *Dow

Chemical*

2. Wei-Fan Kuan - Interfacial-Modified Block Polymers for Lithium Battery Electrolytes - 05/21/2015

Changes in research objectives (if any):

None.

Change in AFOSR Program Manager, if any:

None.

Extensions granted or milestones slipped, if any:

6-month no-cost-extension due to personnel turnover.

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, \$K)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

Report Document

Report Document - Text Analysis

Report Document - Text Analysis

Appendix Documents

2. Thank You

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